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Short communication

Lanthanide chain assembled in metal–organic frameworks: Slow relaxation of the magnetization in Dy(III) and Er(III) complexes

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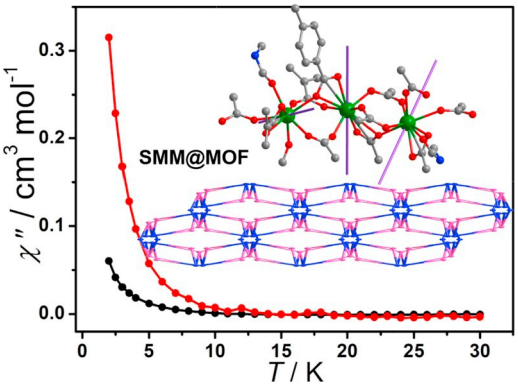
GRAPHICAL ABSTRACT

Three new Ln^{III}-MOFs have been synthesized by employing a trigonal N-containing tricarboxylate ligand. The coordination geometries around the central metal ions exhibit different deviations from ideal square antiprism (D_{4d} symmetry) because of the coordinated solvent molecules. The ac magnetic susceptibility data is consistent with single chain magnet behavior for Dy(III) and Er(III) complexes, which have been studied by the noncritical scaling theory.



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ABSTRACT

Three new Ln^{III}-MOFs, $\{[Dy_{1.5}(TAPB)_{1.5}(DMF)]\cdot 9DMF\}_n$ (Ln = Dy (**1**), Er (**2**), Ho (**3**); TAPB = 4, 4′, 4″-(triazine-2, 4, 6-triyl-tris-(benzene-4, 1-diyl)) tribenzoate), have been synthesized via a solvothermal method by using a trigonal N-containing tricarboxylate as the ligand. The coordination geometries around the central metal ions in the MOFs exhibit different deviations from ideal square antiprism (D_{4d} symmetry) because of the coordinated solvent molecules. The ac magnetic susceptibility data is consistent with single chain magnet behavior for Dy(III) and Er(III) complexes, which have been studied by the noncritical scaling theory.

Lanthanide ions have been widely used for single-molecule magnets (SMMs) which can be potentially applied in ultra-high-density information storage, quantum computing and molecular spintronics [1–4], owing to their high magnetic moments and significant magnetic anisotropy, especially for Kramer's Dy^{III} ion [5,6]. The recent landmark finding by scientists is a mononuclear Dy^{III} SMM possessing high magnetic hysteresis (80 K) and effective energy barrier (1541 cm^{-1}) [7] which shows the great potential of Ln-SMMs in the application of molecule-based magnetic materials. Hence, great interest toward getting high performance Ln-SMMs has been growing recently. However, the

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magnetic dynamics of most Ln-SMMs are still far from satisfactory. There are still many issues and factors unsolved among which the magnetic-structural correlations is a factor that cannot be ignored [8–12]. The geometry of the central metal ions and charge distribution on metal site combined with theoretical calculations to illustrate the structural effect on the magnetic properties, and this has been well-demonstrated in discrete molecules [7,13–20].

On the other hand, metal-organic frameworks (MOFs), as a new generation of materials, has been flourishing in recent years due to their potentially highly porous nature and extraordinary structural diversity [21–23]. MOFs are porous crystalline materials constructed by metal nodes and organic linkers. They have shown promising applications in gas storage and separations, catalysis and chemical sensing [24–34]. However, the use of magnetic units in MOFs has not been well demonstrated. In comparison with the discrete systems, there are many advantages in studying magnetism in MOFs, such as affecting magnetic properties by exchanging the guest molecule [35,36] or by incorporating SMMs into the porous cavities of magnetic MOFs [37]. Another possibility is to control and constrain the coordination environment in Ln(III) MOFs, aiming to attain maximum axial anisotropy [12]. In addition, choosing a suitable ligand can also achieve the dilution effect. Given the fact that Ln(III) MOFs form by self-assembly, this last points are difficult to control because of its large ionic radius and high coordination numbers. In this contribution, we present a new strategy to constrain the coordination geometry around metal centers in a high dimensional molecular system, namely, metal–organic frameworks (MOFs), which contains one dimensional chain in the rigid frameworks. Furthermore, the magnetic-structural correlations have also been discussed in this work.

Three new MOFs material have been obtained via the solvothermal method, namely, $\{[Dy_{1.5}(TAPB)_{1.5}(DMF)]\cdot 9DMF\}_n$ (Ln = Dy (**1**), Er (**2**), Ho (**3**); TAPB = 4, 4′, 4″-(triazine-2, 4, 6-triyl-tris-(benzene-4, 1-diyl)) tribenzoate). The frameworks are formed by helicoidal chains of the Ln (III) ions linked by the tridentate ligand H_3TAPB. The repeating motif in the chain consists of three lanthanide ions. In addition, compound **1** shows slow magnetic relaxations under zero dc field.

A mixture of the organic ligand H_3TAPB and $Ln(NO_3)_2\cdot 6H_2O$ (Ln = Dy, Ho, Er) in a molar ratio of 3:5 was solvothermally reacted in a mixed DMF and 1, 4-dioxane solution at 150 °C to form colorless block crystals of **1**–**3**, which crystallized in the space group $C222_1$ (ESI†). Powder X-ray diffraction (PXRD) measurements support there stability in air atmosphere and high phase purity (Fig. S2). The single crystal X-ray diffraction analyses reveal that they are isostructural. Here, only the structure of **1** is described in detail. The asymmetric unit contains three Dy^{III} ions (Dy1, Dy1A and Dy2 in the crystal structure) with two alternating bridging modes: Dy1-Dy1A are bridged by one *syn*, *syn*-carboxylic and two *syn*, *anti*-carboxylic groups from the TAPB ligand. The two ions Dy1 and Dy1A are eight coordinated by four oxygens from *syn*, *syn*-carboxylate groups, three μ_2–bridging carboxyl oxygen atoms and one oxygen from a DMF molecule. The Dy1-Dy1A distance is 3.9361 Å and the Dy1-O-Dy1A angle (where O is the monoatomic oxygen bridge from the *syn*, *anti*-carboxylato) is 106°. Dy1-Dy2 are bridged by two *syn*, *syn*-carboxylic and one *syn*, *anti*-carboxylato groups from TAPB. Dy2 is octacoordinated by four oxygen atoms from two *syn*, *syn*-carboxylato and four oxygen atoms from two *syn*, *anti*-carboxylic groups. The Dy1-Dy2 distance is 4.2252 Å and the Dy1-O-Dy2 angle (where O is the monoatomic oxygen bridge from the *syn*, *anti*-carboxylato) is 113°. The continuous symmetry measure (CSM) method [38,39] was employed to analysis the local coordination symmetry of the Dy^{III} ions. According to the calculated CSAPR-9 parameter, the minimum of the deviation from an ideal mode is square antiprismatic (D_{4d}) with shape value of 1.189 and triangular dodecahedron (D_{2d}) with shape value of 2.949 for Dy1 and Dy2, respectively (Fig. 1a, b and Table S2). The repeating three nuclear Dy(III) unit form one helicoidal chain bridged by the carboxyl (Fig. 2). Then the one helicoidal chains are connected by the ligand to form a 6, 6, 6, 6-connected three-dimensional framework with a point symbol of [4.4.4.4.4.4.4(2).4(2).4(2).4(2).6(6).6(10).6(10).6(12).6(12)] (Fig. S3).

For $[Ln_2(RCOO)_3]$ with Ln = Dy a Cambridge Structural Database (version 5.39 updates, Feb 2018) search yields 27 hits. The Dy-Dy distances found in the complexes reported here are 4.2 Å on average, in the 3.9 to 5.2 range found in the 27 hits in the CSD for $[Ln_2(RCOO)_3]$. A trend is observed: with more *syn*, *syn*-carboxylato bridges a longer Ln-Ln distance is observed. The *syn*, *syn*-carboxylato bridges and larger Ln-O-Ln angles will results in antiferromagnetic coupling. However, even if the two exchange couplings, as shown in Fig. S4 are maybe antiferromagnetic and the polymer will have a net magnetic moment for each trinuclear unit.

Direct current (dc) magnetic susceptibility data for the three complexes **1**–**3** were collected at 0.3 T applied field from 2 K to 300 K (Fig. S4). The $\chi_M T$ values at 300 K are 42, 33 and 42 $cm^3\,K\,mol^{-1}$ for MOFs **1**, **2** and **3**, respectively, which are very close to the expected values of 42.5, 34.43, 42.19 $cm^3\,K\,mol^{-1}$ for three non-interacting Dy^{III}, Er^{III} and Ho^{III} ions (Dy^{III}, $^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$ and $g_J = 4/3$; Er^{III}, $^4I_{15/2}$, $S = 3/2$, $L = 6$, $J = 15/2$ and $g_J = 6/5$; Ho^{III}, $^5I_8$, $S = 2$, $L = 6$, $J = 8$ and $g_J = 10/8$). Upon lowering the temperature, the $\chi_M T$ value decreases for **1**–**3**, the shape of the $\chi_M T$ product curve is typical of lanthanide ions with strong spin orbit coupling and it suggests that there may be the antiferromagnetic interactions in **1**–**3** [40–43]. As can be seen in Fig. S4, both data sets overlap, except for **2**. Below 30 K an additional data set was collected with an applied fields of 195 Oe for **2**. There is an increase at temperatures below 10 K for the lower dc field (the inset of Fig. S4). This indicates net spins in **2**. The magnitude of the interactions in MOFs **1** and **2** can be estimated by the noncritical scaling theory using the sum of two exponential functions: $\chi T = C_1 \exp.(E_1/T) + C_2 \exp.(E_2/T)$, in which $C_1 + C_2$ is the extrapolated Curie constant at room temperature while E_1 and E_2 represent the magnitudes of intrachain magnetic interactions and the crystal-field contributions (Fig. 3a and Fig. S5) [44–46]. The negative E1 and E2 value of −31.22 and −0.86 cm^{-1} **1**, indicates that the antiferromagnetic interactions between Ln^{III} ions in it with the field of 3000 Oe. The values of C_1 and C_2 are 6.34(2) and 36.87(9) $cm^3\,K\,mol^{-1}$ for **1**, respectively. However, a negative E1 and a small positive E2 value of −20.28(1) and 0.56(6) cm^{-1} for **2** with an applied fields of 195 Oe below 30 K and 3000 Oe above 30 K suggests the weak but nonnegligible ferromagnetic interactions between Er^{3+} ions at low temperature (Fig. 3b).

As can be seen from Fig. S5, the field dependence of the magnetizations for **1**–**3** has been determined at 2.0 K in the range of 0–50 kOe. The magnetization values rise abruptly at low fields and reach 17.93 Nβ for **1**, 14.76 Nβ for **2** and 15.98 Nβ for **3** at 50 kOe, much lower than the theoretical saturation values due to the presence of magnetic anisotropy, crystal-field effect, or low-lying excited states [47–49]. The rapid growth of the magnetization vs. field plot at 2 K is also consistent with a net magnetic moment for the trinuclear unit and thus, for the one-dimensional polymer.

In addition, ac magnetic susceptibility data were collected below 30 K at various frequencies with and without dc field in order to study the dynamic magnetic properties of **1**–**3**. **1** showed a significant frequency dependence of out-of-phase signals under zero dc field, strongly suggesting the presence of slow relaxation of the magnetization (Fig. 4, Fig. S6 and Fig. S7) [50]. However, the χ″ peaks are not observed in the temperature ranges available. Upon application of a dc field of up to 2000 Oe no χ″ maxima were observed, suggesting the presence of a fast relaxation that results from QTM. In a real system, even in Kramer's systems, QTM can be induced by many factors such as dipolar coupling interactions or environmental distortions [51]. In this system, the coordination geometries are deviating from ideal D_{4d} for the central metal ions, so there should be a transverse anisotropy. As shown in Fig. 5, **2** showed out-of-phase ac signals only under applied dc fields. **3** did not show any signal in the out-of-phase ac magnetic susceptibility. Given the one-dimensional nature of **1**–**3** and considering that the chains are effectively isolated in the MOF consistent with a shortest chain-chain

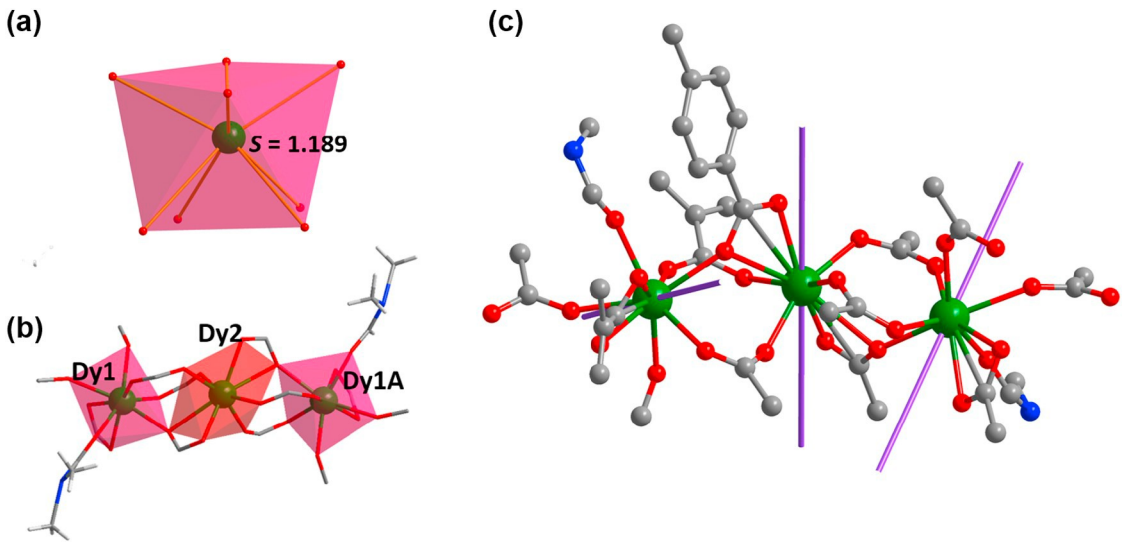

Fig. 1. (a) The coordination environments of the Dy_1; (b) The trinuclear Dy unit; (c) Principal magnetic axis (purple line) for **1**. The anisotropy axes have been calculated using a purely electrostatic model, see text for details. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

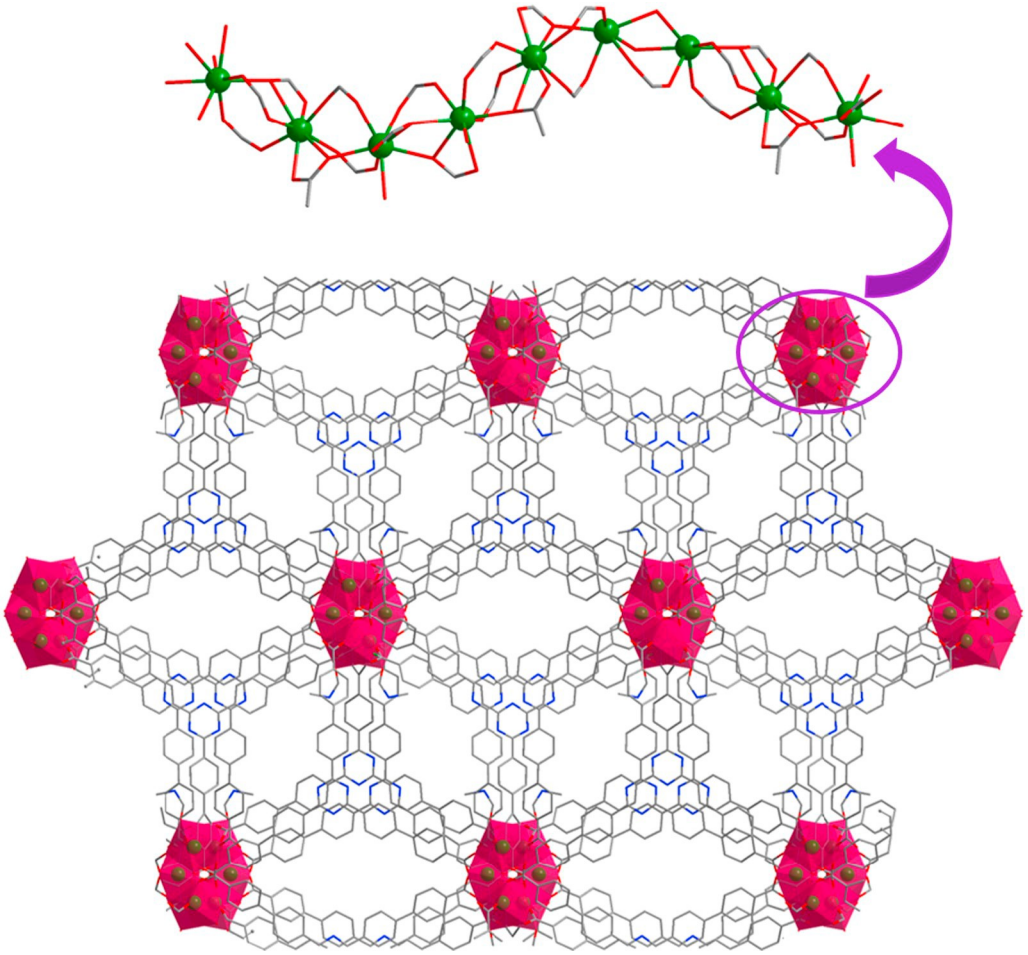

Fig. 2. One-dimensional helicoidal chain bridged by carboxyl and the three-dimensional framework of **1**.

distance of circa. 2 nm. The ac magnetic susceptibility data is consistent with single chain magnet behavior for **1** and **2**, in agreement with the result of the noncritical scaling theory. However, without magnetic data below 1.8 K that can ascertain the frequency dependence of the relaxation, magnetic ordering of the chains cannot be ruled out.

In order to study the correlation between the structure and the magnetic, the ground state magnetic anisotropy axis of Dy^{III} was obtained by the program Magellan (Fig. 1c and Fig. S8) [9]. The results show that the principal axises of Dy1 and Dy2 both lie along the shortest DyeO bond direction. The Dy1-Dy2 are bridged by two *syn*,

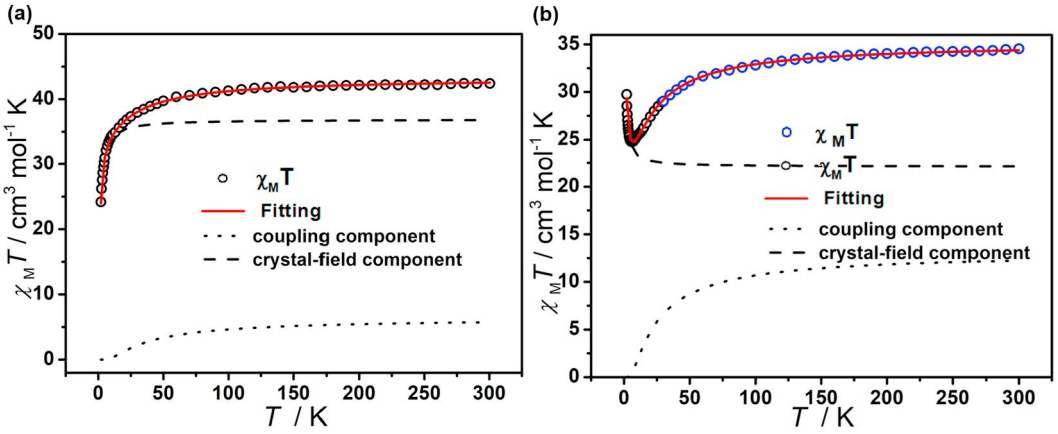

Fig. 3. Temperature-dependent magnetic susceptibilities of **1** (a) and **2** (b). The fitting lines are obtained from the scaling model (red line), the coupling effect (dotted line), and the crystal-field component (dash line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

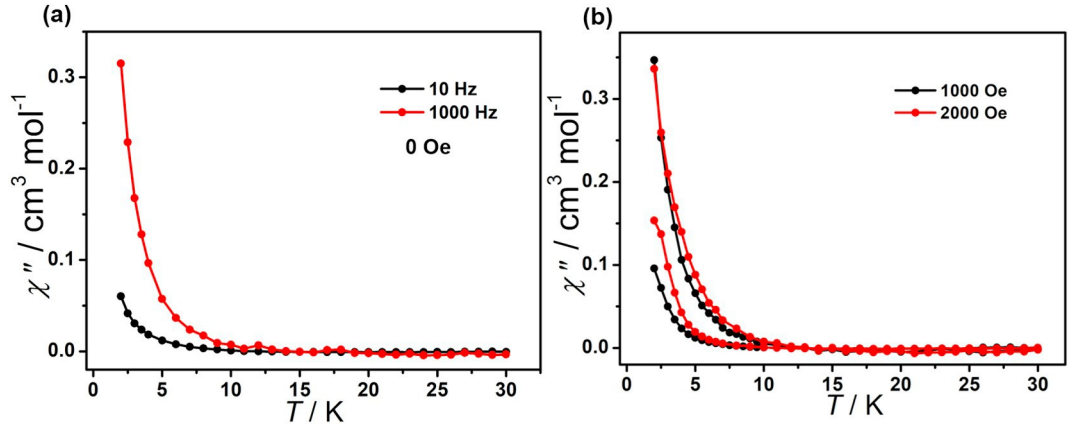

Fig. 4. Ac magnetic susceptibility at 100 and 1000 Hz for **1** at zero dc field (a) and 1000, 2000 Oe (b).

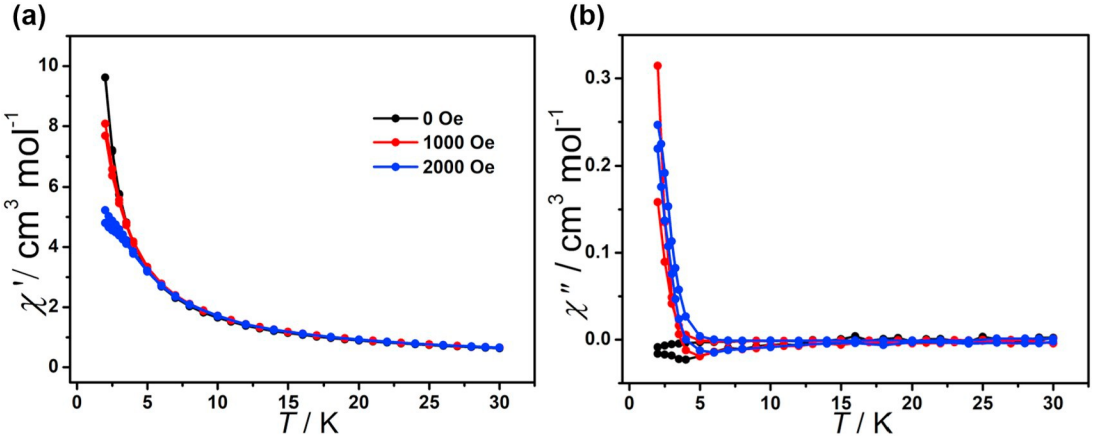

Fig. 5. Ac magnetic susceptibility at 100 and 1000 Hz for **2** at the indicated applied fields.

syn-carboxylato and one *syn*, *anti*-carboxylato groups from TAPB. This coordination mode results in an almost perpendicular magnetic axises in agreement with the ac data that suggests small, non-axial magnetic anisotropy.

In conclusion, three new 3D frameworks containing interesting one-dimensional chains have been structurally and magnetically studied. Single crystal X-ray analyses reveal that MOFs **1**, **2** and **3** are isomorphous, each TAPB ligand act as a trigonal ligand to link the Ln^{III} ions. Magnetic studies reveal that Dy^{III} MOF shows slow relaxation of the magnetization under zero dc field. This work illustrated a new strategy to obtain SMM by combining the research fields of both molecular nanomagnets and MOFs.

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Appendix A. Supplementary material

CCDC 1874736-1874738 (**1–3**) contains the supplementary crystallographic data for the title compounds. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2019.02.005.

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